

HAN-Based Monopropellant Technology Development
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ABSTRACT

NASA Glenn Research Center is sponsoring efforts to develop technology for high-performance, high-density, low-freezing point, low-hazards monopropellant systems. The program is focused on a family of monopropellant formulations composed of an aqueous solution of hydroxylammonium nitrate (HAN) and a fuel component. HAN-based monopropellants offer significant mass and volume savings to small (< 100 kg) satellite for orbit raising and on-orbit propulsion applications. The low-hazards characteristics of HAN-based monopropellants make them attractive for applications where ground processing costs are a significant concern. A 1-lbf thruster has been demonstrated to a 20-kg satellite orbit insertion duty cycle, using a formulation compatible with currently available catalysts. To achieve specific impulse levels above those of hydrazine, catalyst materials that can withstand the high-temperature, corrosive combustion environment of HAN-based monopropellants have to be developed. There also needs to be work done to characterize propellant properties, burning behavior, and material compatibility. NASA is coordinating their monopropellant efforts with those of the United States Air Force.

INTRODUCTION

Since 1996, NASA Glenn Research Center has been sponsoring technology efforts to advance the state of monopropellant propulsion technology. The goal is to develop monopropellant propulsion systems with significantly better performance, thermal, and hazard properties than the state-of-art monopropellant, hydrazine (N_2H_4). The technology efforts have focused on a family of monopropellant formulations consisting of an aqueous solution of hydroxylammonium nitrate (HAN), which serves as the oxidizer, and a fuel component. HAN usually composes the majority of the formulation and dominates the characteristics of the monopropellant. Generically, HAN-based monopropellants are at least 40 percent denser than N_2H_4 , have freezing points less than $0^\circ C$, have no vapor hazard, and do not require any extraordinary storage, handling, or disposal procedures. The selection of the fuel component and relative percentage of HAN, fuel, and water determine the combustion temperature and, therefore, performance.

The primary application targeted for HAN-based monopropellants is orbit raising of small (≤ 100 kg) satellites^{1,2}. For these and other small ΔV applications, propulsion options are limited to low-performing, high-volume cold gas systems, bulky (and single-shot) solid rocket motors, or N_2H_4 systems. HAN-based monopropellants offer a small envelope system without the extensive thermal management and hazardous (and costly) servicing operations associated with N_2H_4 . Depending on the formulation, HAN-based monopropellants can offer higher specific impulse (Isp) performance than N_2H_4 . The current NASA-sponsored HAN technology effort has an Isp goal of 250 sec (@ 200 psia chamber pressure and 50:1 area ratio). Figure 1 shows the benefits of HAN to a 100-kg satellite, as well as illustrates the technology development path.

HAN-based monopropellants can be used in other roles currently filled by N₂H₄ systems, such as the attitude control systems for expendable launch vehicles³, satellite on-orbit propulsion⁴, and gas generators. Its non-toxic, high-density nature makes it well suited for Shuttle-launched payloads⁵ and small, manned spacecraft⁶. Its low freezing point (and therefore, little or no active thermal management) provides benefit to power-limited applications, such as for planetary atmospheric maneuvers⁷. For formulations with Isp levels above 270 sec, HAN-based monopropellants could also be used in applications traditionally filled by bipropellants. The reduced servicing costs offered by HAN-based monopropellants are particularly attractive for use in the reaction control systems (RCS) of reusable launch vehicles (RLV's). HAN-based monopropellants would provide a single-propellant (fewer components to service), ambient-temperature liquid (no thermal management), low-hazard (no area clear operations or hazardous procedures) RCS that could reach the two orders of magnitude cost reduction goal sought by 3rd Generation RLV's. Figure 2 illustrates the generic benefits of HAN-based monopropellant technology and potential applications.

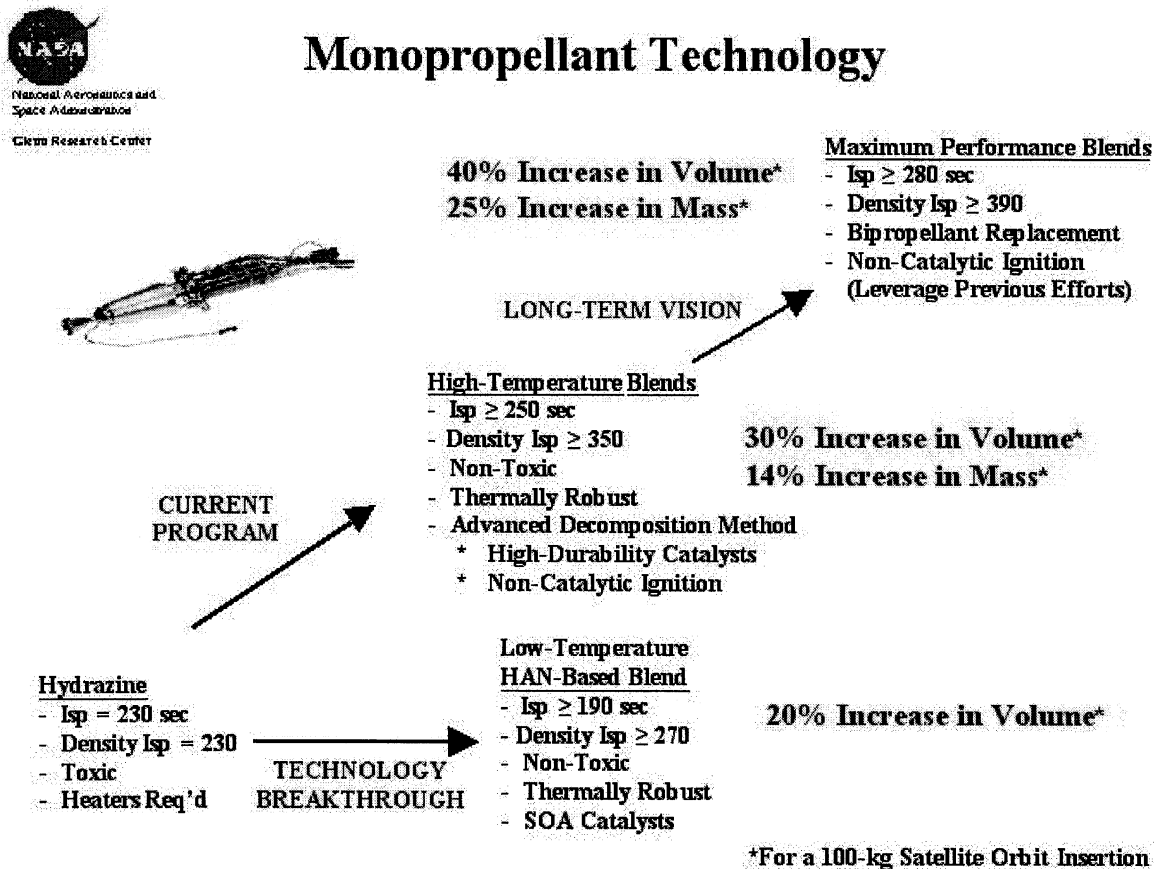
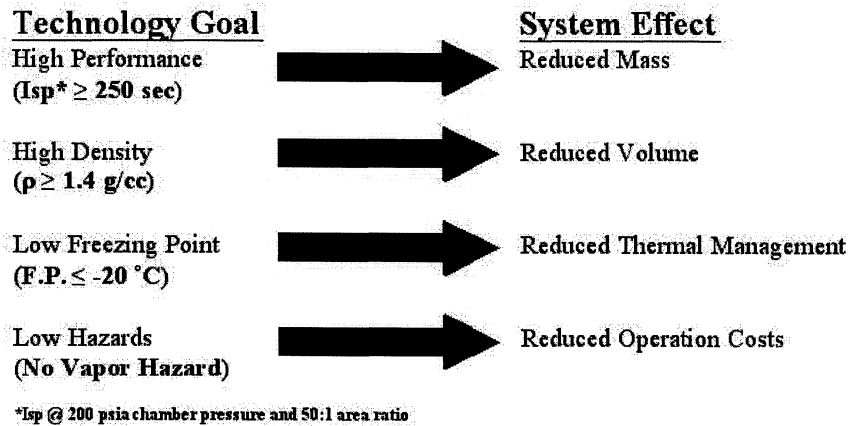


Figure 1: Advanced Monopropellant Technology Benefits to Small Satellite Propulsion

Monopropellant Technology



Applications:

- High-performance, small-envelope system for orbit insertion of small satellites (≤ 100 kg)
- High-performance, small-envelope system for on-orbit propulsion of satellites
- Low-maintenance RCS for reusable RLV and ACS for ELV/ICBM
- Non-toxic system for Shuttle-launched payloads
- High-performance, non-toxic system for small, manned spacecraft
- High-performance, low-temperature system for planetary atmosphere maneuvers

Figure 2: HAN-Based Monopropellant Benefits and Applications

HAN-BASED MONOPROPELLANT TECHNICAL CHALLENGES

HAN-based monopropellants have their genesis in an Army program to develop liquid gun propellants (LGP) as insensitive munitions⁸. When the monopropellant technology effort started, there was a formidable challenge in adapting a class of propellants originally developed as munitions for large guns (operated at 50,000 psi) for use in satellite propulsion systems (operating less than 400 psi). The primary LGP formulation was XM46, which used triethanolammonium nitrate (TEAN) as the fuel component. However, in rocket testing, XM46 did not provide acceptable combustion characteristics at pressures less than 500 psi⁹. Other fuel components would have to be examined for spacecraft propulsion applications.

Since HAN-based monopropellants are actually mixtures of an aqueous oxidizer and a fuel, its decomposition and combustion is much more complex than single molecular entities such as N₂H₄ or hydrogen peroxide. HAN first decomposes into hydroxyl amine and nitric acid, which then reacts with the fuel. The decomposition process and burning behavior is not well understood for HAN-based monopropellants at the pressures (< 400 psia) needed for the spacecraft application. The combustion environment for HAN-based monopropellants is harsh. Because the molecular weight of its exhaust products are higher than in N₂H₄, HAN-based monopropellants must operate at higher temperatures to achieve the same performance. To achieve $I_{sp} \geq 250$ -sec performance goals, the catalytic reactor will experience temperatures above 1700 °C. The decomposition process produces nitric acid as a combustion intermediate. The combustion products include steam and carbon dioxide. The current state-of-art monopropellant catalyst (Shell 405, iridium on alumina substrate) can not withstand this high-temperature, corrosive decomposition environment for the lifetimes needed for most satellite

propulsion applications (multiple hours). The technology development tasks for HAN-based monopropellants are summarized in Figure 3.

HAN-Based Monopropellant Development

- **Propellant**
 - Formulation Optimization
 - Property Characterization
 - Health/Hazards Characterization
 - Storage Stability
- **Ignition**
 - High-Temperature, High-Durability Catalysts
 - Catalyst Bed Optimization
 - Non-Catalytic Ignition
- **Combustion**
 - Decomposition Mechanisms
 - Burning Behavior
- **Thrust**
 - Chamber Material
 - Injector Optimization
 - Thermal Interface
- **System**
 - Material Compatibility
 - Propellant Tank Design

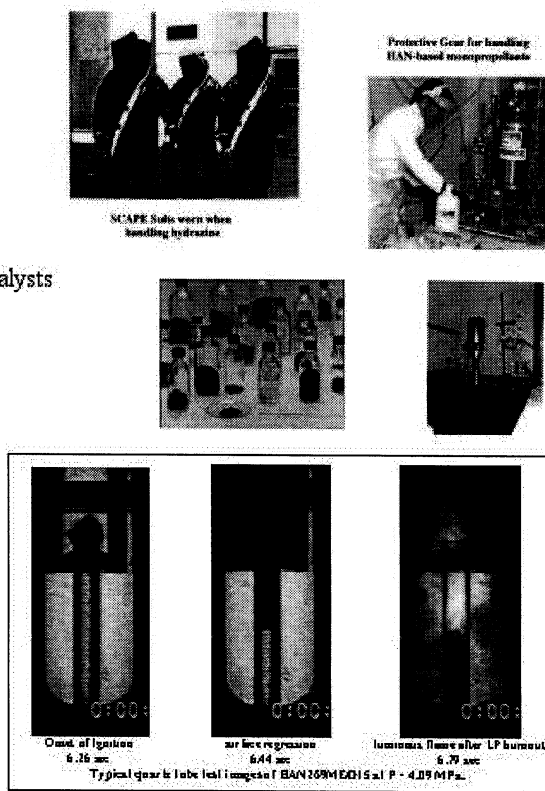


Figure 3: Development Tasks for HAN-Based Monopropellants

HAN-BASED MONOPROPELLANT DEVELOPMENT EFFORTS

Aerojet-Redmond Rocket Center (RRC) has conducted much of the HAN-based monopropellant technology work (Aerojet-RRC is the former Primex Aerospace Company). Aerojet-RRC screened candidate fuels suitable for space propulsion applications and then characterized the properties, storage stability, and combustion behavior of several resultant formulations^{10, 11}. Table I shows a comparison of two HAN-based monopropellant formulations to N₂H₄.

It was decided to focus on a formulation compatible with state-of-art catalysts, meaning it would have a lower Isp than N₂H₄, though it would still provide a volume benefit (Figure 2). This approach would allow focus on propellant and thruster development, without simultaneously entering a lengthy catalyst material development effort. Furthermore, even this “low-temperature” HAN formulation would provide ground processing and volume benefits that would be important to small satellite users. A formulation (HAN204GLY14) using glycine as a fuel and excess water to keep combustion temperatures down to 1100 °C was selected for

development. This resulted in a projected delivered Isp of 190 sec for the formulation (93% of the theoretical Isp of 204 sec). A storage stability issue for the HAN204GLY14 blend was addressed by the addition of stabilizers that provided for long-term storage (years) at temperatures up to 65 °C¹¹. The stabilized version of HAN204GLY14 did not differ in combustion performance from the unstabilized version.

	N2H4	“Low-Temperature” HAN-Glycine	High Performance HAN-Methanol
Current TRL	9	5	3
Delivered Isp*	230 sec	190 sec	≥ 250 sec
Density-Isp	230	266	≥ 350
Freezing Point	0 °C	-20 °C	< -20 °C
Toxic Vapor Hazard?	Yes	No	No
Combustion Temperature	1000 °C	1100 °C	≥ 1650 °C
Decomposition Environment	Ammonia, Hydrogen	Nitric Acid (Intermediate), Carbon Dioxide, Steam	Nitric Acid (Intermediate), Carbon Dioxide, Steam

*At chamber pressure = 200 psia and area ratio = 50

Table I: Monopropellant Comparison

A 1-lbf, HAN thruster was designed and different active metals, bed configurations, and injector designs were tested^{12, 13}. The 1-lbf thruster, using the HAN204GLY14 blend, was tested to a duty cycle appropriate for orbit insertion of a 20-kg satellite (Figure 4). This represented the first major advance in monopropellant technology in over two decades. The thruster accumulated over 8000 seconds of operation, firing primarily in steady-state mode. The thruster was operated in blowdown mode to simulate a satellite propulsion system. There was approximately 7.5% degradation in chamber pressure (and therefore, thrust) from the first and last test (conducted as the same feed pressure). Pulse testing was also conducted, though the use of a facility valve affected impulse bit repeatability.

At the start of the technology program, an effort was simultaneously sponsored at Thiokol, Elkton Division. Thiokol focused on larger thrust applications (100- to 1000-lbf), using the LGP formulations. A successful firing (using a pyrotechnic ignition system) of a heavyweight engine was achieved, running a formulation (LGP 1898) that used diethylhydroxylammonium nitrate (DEHAN) as the fuel. The engine operated up to a chamber pressure of 700 psia and was projected to have an Isp of 270 sec (at 50:1 area ratio)¹⁴. The Thiokol effort had to be halted due to funding constraints.

Aerojet RRC’s current NASA-sponsored effort is focusing on high-performance (Isp ≥ 250 sec) formulations. A number of high-performance formulations were tested in a catalytic reactor (since Shell 405 was used, firings were limited to a couple of seconds duration)¹⁵. Blends with theoretical performance up to 288-sec Isp have been tested (delivered Isp is expected to be at least 93% of theoretical). Methanol has emerged as the leading candidate fuel for these high-performance blends. Tris(aminoethyl)amine trinitrate (TREN3) is also being investigated as a fuel component.

The primary challenge of this effort is to develop a long-life catalyst system that can provide the same long-life characteristics needed for spacecraft propulsion applications. RRC is using laboratory-scale testing to screen a large number of candidate catalyst materials, in terms of reactivity with candidate HAN formulations and in terms of durability in simulated HAN combustion environments^{16,17}.

Low-Temperature HAN-Glycine Thruster Demo

- Demonstrated 1-lbf Thruster Using Stabilized HAN-Glycine (w/ Excess Water) Blend
 - Different Active Metals, Bed Configurations, and Injectors Examined
 - Final Configuration: Thermally-Conditioned Shell 405 Catalyst w/ Penetrating Injector
 - Thruster Tested to Duty Cycle for Orbit Insertion of 20-kg Satellite
 - Accumulated 8000 Seconds in 21 Cold Starts Over Full Feed Pressure Range
 - 600 °F Preheat was Minimum for Smooth Combustion
 - Limited Pulse Testing Also Conducted

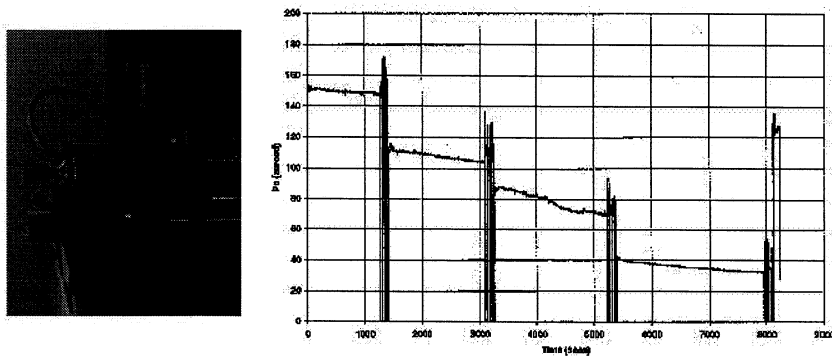


Figure 4: 1-lbf Thruster Demonstration with “Low-Temperature” HAN-Glycine Blend

The Air Force Research Laboratory (AFRL) at Edwards Air Force Base, currently has a HAN-based monopropellant thruster technology program, called the Liquid Engine Advanced Propellant Development Program (LEAP-DP). An AFRL-developed HAN formulation¹⁸ is being used for LEAP-DP, which is targeted for higher thrust and shorter lived applications than the NASA program. Aerojet-RRC is conducting the LEAP-DP development effort for the USAF. Coordination of NASA and USAF monopropellant efforts is facilitated by a joint DoD-NASA organization, Integrated High Payoff Rocket Propulsion Technology (IHRPT). The IHRPT Materials Working Group (IMWG) was formed to specifically address deficits in materials technology in the IHRPT regime. Under IMWG, there are two efforts funded to develop high-temperature, high-durability catalyst materials. Recently, two more efforts were started to develop chamber materials that are suitable for the HAN combustion environment. Also, there are catalytic and non-catalytic ignition technology efforts being conducted under Small Business Innovative Research (SBIR) programs sponsored by NASA and USAF. IMWG and SBIR efforts are expected to feed ignition and chamber material solutions to the NASA and USAF thruster development programs.

The Pennsylvania State University is conducting combustion experiments with HAN-based monopropellants to better understand its decomposition mechanisms and burning behavior. This work was done initially as a subcontract of the RRC program, focusing on the satellite propulsion blends¹⁹. Later, the 3rd Generation RLV program sponsored a grant to investigate the

behavior of blends appropriate for RCS applications ($I_{sp} \geq 270$ sec)²⁰. Using a liquid propellant strand burner device, the burn rates of the HAN formulations were determined. Fine-wire thermocouples were used to measure the temperature distribution in the reaction zone. Chemical analysis of the recovered combustion products and the pyrolysis products of fresh formulations were conducted to better understand the chemical processes. Catalysts are being incorporated into the strand burning tests to assess the affect of its presence on burning behavior.

The majority of HAN compatibility work has been done in the liquid gun propellant programs with XM46²¹. There has also been HAN compatibility work conducted in gas generator programs and the monopropellant development effort. Despite these efforts the HAN compatibility database is far from complete and sometimes unclear, because of differing ways of conducting tests and interpreting results. GRC is conducting an in-house material compatibility, focusing on 300-series stainless steel²². Other HAN material compatibility efforts are likely being conducted by industry. Currently, there is a technology deficit concerning HAN-based system components. It is known that HAN is not compatible with silica-containing materials, such as the state-of-art tank bladder elastomer, AFE-332. Finding a suitable tank design, using either a compatible elastomer material for the bladder or an alternative delivery system, is critical in implementing HAN-based monopropellant systems.

SUMMARY

HAN-based propellant formulations are being developed to provide high-performance, high-density, low-freezing point, low-hazards monopropellants. HAN-based monopropellants offer significant benefits to limited-volume, low ΔV applications (such as small satellite orbit raising) and to applications where ground processing costs are important (such as RCS for future RLV's). A 1-lbf thruster has already been fired to a small satellite orbit insertion duty cycle, using a formulation compatible with currently available catalysts. High-performance HAN formulations will require the development of high-temperature, high-durability catalyst materials capable of long-life operation in the harsh HAN combustion environment. NASA and USAF efforts are being leveraged to develop these catalyst material systems. There is also work being conducted to characterize propellant properties, combustion behavior, and material compatibility.

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